

# Thermodynamic Modeling of AZ-101 Slurry Leaching

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April 2003

WTP  
Project  
Report

Prepared for Bechtel National, Inc.  
Under contract 24590-101-TSA-W000-0004

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Battelle – Pacific Northwest Division  
Richland, Washington 99352

## ***Completeness of Testing***

*This report describes the results of work and testing specified by TSP-W375-01-0005 Rev. 0 and TP-RPP-WTP-099 Rev 1. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.*

### **Approved:**

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Gordon H. Beeman, Manager  
WTP R&T Support Project

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Date

## Summary

This document describes work performed under Battelle – Pacific Northwest Division (PNWD) Test Plan TP-RPP-WTP-099 Rev 1 in support of the River Protection Project–Waste Treatment Plant (RPP-WTP). The results from sludge leaching studies of Tank AZ-101 waste samples were modeled using the Environmental Simulation Program (ESP) v6.6 (OLI Systems Inc. 2002). The ESP simulations were conducted using both the Pitzer (Felmy) database and the Bromley Zematis version (Nuclear) database. ESP simulations using the two different databases were in reasonably good agreement for the majority of the components but differed significantly for some of the minor components (phosphate, lanthanum, neodymium). The models predict that the solids present in the slurry were comprised predominately of oxide/hydroxide phases with only minor amounts of carbonate and sulfate. With the exception of aluminum hydroxides, these oxide/hydroxide phases are predicted to remain insoluble during treatment. The principal anions in solution, nitrate ( $\text{NO}_3^-$ ) and ( $\text{NO}_2^-$ ), were predicted to be completely soluble.

Significant amounts of aluminum are predicted to dissolve in the leach step. The models predict that if the aluminum is present in the initial slurry as the more soluble gibbsite phase, then all of the aluminum should be completely removed at the experimental temperature of 85°C. However, if the aluminum is present as the more insoluble boehmite phase, then aluminum should be only partially soluble. The minor amounts of precipitated sulfate, fluoride, and oxalate predicted to be initially present in the sludge are removed in the first wash step. In general, the calculated supernatant concentrations followed the same trends observed experimentally and were often quite close quantitatively to the experimental values. Based upon these results, several recommendations are made on how to process AZ-101 sludge more efficiently. These recommendations include: 1) eliminating the second wash step and possibly eliminating the wash process entirely, 2) adjusting the reaction time in the leach step to enhance any removal of soluble gibbsite, 3) testing higher hydroxide concentrations in the leach step in order to remove the boehmite, and 4) using a higher base concentration in the rinse steps to suppress the tendency for aluminum hydroxide post-precipitation.

PNWD implemented the RPP-WTP quality requirements in the Quality Assurance Project Plan, RPP-WTP-QAPjP, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP).

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. The review procedure is part of the PNWD's WTPSP manual.

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## Glossary of Terms and Acronyms

ESP	Environmental Simulation Program
FFS	Fluor Federal Services
HLW	High-Level Waste
PNWD	Battelle – Pacific Northwest Division
RPP-WTP	River Protection Project–Waste Treatment Plant

## Mineral Names and Formulae

<b>Mineral Name</b>	<b>Formula</b>
Boehmite	$\gamma\text{-AlOOH}$
Barite	$\text{BaSO}_4$
Calcite	$\text{CaCO}_3$
Gibbsite	$\beta\text{-Al(OH)}_3$
Goethite	$\text{FeOOH}$
Hydroxyapatite	$\text{Ca}_5\text{OH(PO}_4)_3$
Pirssonite	$\text{Na}_2\text{Ca(CO}_3)_2 \cdot 2\text{H}_2\text{O}$
Gaylussite	$\text{Na}_2\text{Ca(CO}_3)_2 \cdot 5\text{H}_2\text{O}$

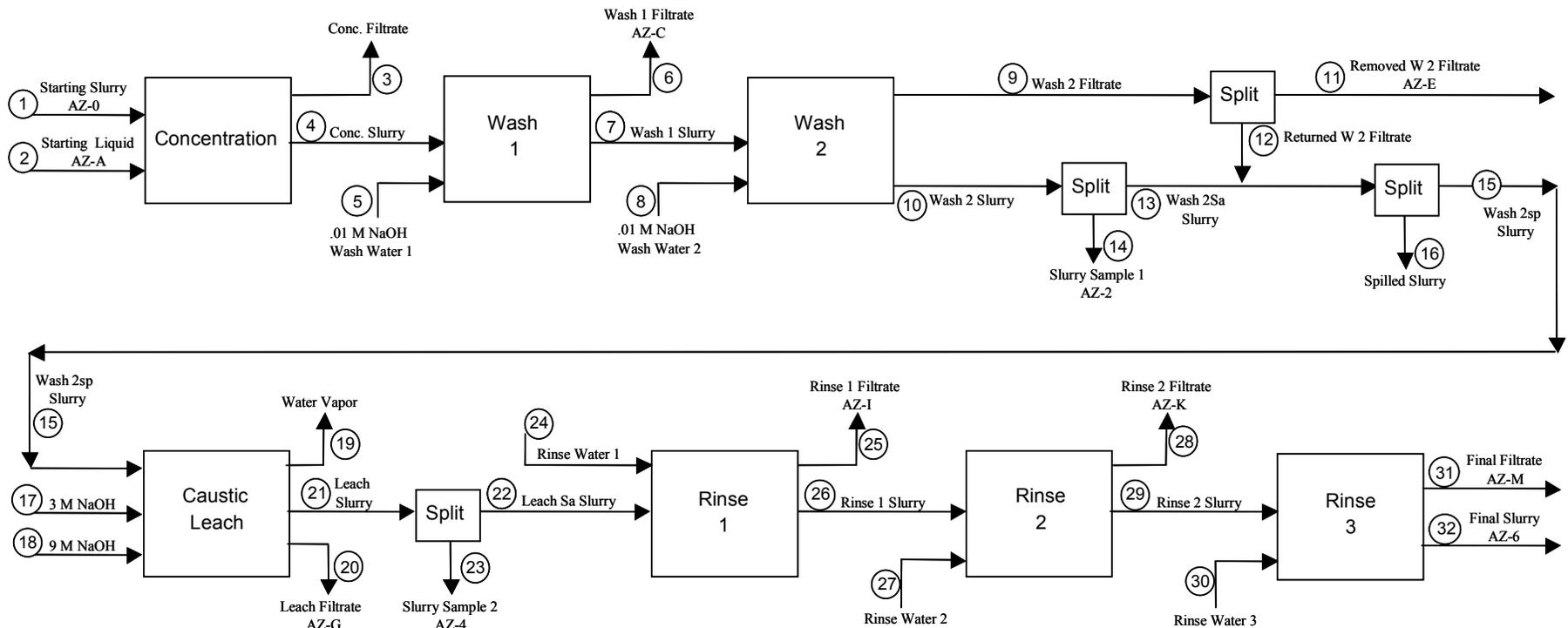
# 1.0 Introduction

Caustic leaching is proposed as pretreatment of the tank waste sludges to reduce glass-limiting components in High-Level Waste (HLW) vitrification. Sludge leaching studies were conducted at this laboratory (Geeting et al. 2002) and consisted of a series of wash, leach, and rinse steps. This report describes the results of thermodynamic modeling of the sludge leaching process for Tanks AZ-101 performed under Battelle – Pacific Northwest Division (PNWD) Test Plan TP-RPP-WTP-099 Rev 1 in support of the River Protection Project- Waste Treatment Plant (RPP-WTP). The thermodynamic modeling studies were performed using the Environmental Simulation Program (ESP) model v 6.6 (OLI Systems Inc. 2002). Additional details on both the sludge leaching process and the thermodynamic models are provided below.

## 1.1 Sludge Leaching Studies

Complete details on the sludge leaching studies are provided in Geeting et al. 2002. Briefly the process consisted of a series of concentration, wash, leach, and rinse steps. The wash and rinse steps were conducted using inhibited water (0.01M NaOH). There were two wash and three rinse steps. The single leach step was conducted using 3M NaOH and at a temperature of 85°C. Both slurry and supernatant samples were taken during various times during the process. These samples represent the experimental data to which the modeling results can be compared. Complete mass balances were maintained during the process including the masses of removed sample for analysis.

A block flow diagram of the complete process with the mass balance is shown in Figure 1.1. This block flow diagram shows the feed concentration, two wash, leach, and three rinse steps as carried out experimentally and simulated with ESP. The simulation was carried out by beginning with the analyses of the initial slurry and supernatant. The component concentrations were then predicted at each step in the process. These predictions were based solely upon the initial slurry composition, the masses of added or removed material, and the equilibrium thermodynamic constraints. No other adjustments or refinements were made to the model.



Stream ->	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Liquid Mass (g)	1563	145	656	1052	1000	1085	969	1000	1074	896	594	480	881	15	1340	20	1116	645	25	1763	1492	1464	28	1200	1361	1246	1200	1235	1209	1200	1216	1192
Solid Mass (g)	294	1	0	295	0	0	293	0	0	291	0	0	286	5	282	4	0	0	0	0	103	101	2	0	0	158	0	0	160	0	0	160
Total Mass (g)	1857	146	656	1347	1000	1085	1262	1000	1074	1187	594	480	1167	20	1622	24	1116	645	25	1763	1595	1565	30	1200	1361	1404	1200	1235	1369	1200	1216	1352
Liquid Volume (mL)	1268	115	530	850	1002	975	870	1002	1018	850	564	455	836	14	1271	19	1012	501	25	1604	1358	1332	25	1203	1276	1168	1203	1196	1171	1203	1198	1174
Solid Volume (mL)	102	0.3	0	103	0	0	102	0	0	101	0	0	100	2	98	2	0	0	0	0	25	24	0.5	0	0	48	0	0	49	0	0	49
Total Volume (mL)	1370	115	530	953	1002	975	972	1002	1018	951	564	455	936	16	1369	21	1012	501	25	1604	1383	1356	26	1203	1276	1216	1203	1196	1220	1203	1198	1223
Wt.% Solids	15.8	0.7	0.0	21.9	0.0	0.0	23.2	0.0	0.0	24.5	0.0	0.0	24.5	25.0	17.4	16.7	0.0	0.0	0.0	0.0	6.5	6.5	6.7	0.0	0.0	11.3	0.0	0.0	11.7	0.0	0.0	11.8
Ionic Strength	6.08	6.79	6.12	6.12	0.01	2.73	2.73	0.01	1.27	1.27	1.27	1.27	1.27	1.27	1.27	1.27	3.01	9.67	0.00	3.37	3.37	3.37	3.37	0.00	1.71	1.71	0.00	0.83	0.83	0.00	0.41	0.41
pH	14.1	14.2	14.2	14.2	12.0	13.6	13.6	12.0	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1	14.6	15.9	7.0	12.7	12.7	12.7	12.7	7.0	14.1	14.1	7.0	13.7	13.7	7.0	13.4	13.4

**Figure 1.1. Block Flow Diagram and Mass Balance for the Tank AZ-101 Sludge Washing Process**

The exact masses of slurry or supernatant removed in each individual step, as well as a definition of the symbols (AZ-0, AZ-E, ...) can be found in Geeting et al. (2002). Studies done at room temperature except for the caustic leach step, which was performed at 85°C. The mass balance and other data are from the simulation with the Nuclear database.

## 1.2 Thermodynamic Modeling

The simulations were run using the ESP model v 6.6. Two different databases were used in the modeling simulations. The first database (Felmy) is based upon the Pitzer equations (Pitzer 1973, 1991). The details on the inclusion of the Pitzer model can be found elsewhere (Sanders et al. 2001). The Felmy database has been developed over the years by the principal author of this report, and the thermodynamic data were detailed in earlier reports (Felmy et al. 1994, Felmy 2000; Felmy and MacLean 2001). The second database (Nuclear) was developed at the Hanford site by G. T. MacLean (the second author of this report) and is based upon the Bromley Zematis approach. The Bromley Zematis approach is documented in the standard references for the ESP model (OLI Systems 2002). The approach of using two different thermodynamic models allows an assessment of the impacts of thermodynamic data on the model predictions.

The initial sodium ( $\text{Na}^+$ ) concentration in the slurry and supernatant was adjusted slightly to match the expected free hydroxide concentration (0.67M) (Urie et al. 2001). The simulation of the leach step was conducted at the experimental temperature of 85°C rather than the final temperature of filtration (~23°C). For constituents that have phases which are more soluble at a higher temperature, e.g., aluminum (Al), an overestimation of the total leachable concentrations could result if precipitation occurred during filtration at the lower temperature. No other adjustments were made to the model inputs.

## 2.0 Results and Discussion

The calculated supernatant concentrations are compared with the experimental results for each of the two wash steps, the single leach step, and the three rinse steps (Figure 1.1). The details on the modeling calculations include each individual component concentration, the predicted dominant aqueous species, and the predicted solid phases, which are given in the Appendix A. The experimental supernatant concentrations are also given in Appendix A for reference. This section presents a summary of the reactive components and solid precipitation issues that effect slurry processing.

### 2.1 Precipitated Solids

Table 2.1 presents a summary of the equilibrium solids calculated in the modeling simulations. This summary includes all phases present in the initial slurry (Table A1) or formed during the wash (Tables A2 and A3), leach (Table A4), and rinse (Tables A5, A6, A7) steps. In general, the models predict that the solids present in the AZ-101 slurry should be composed principally of hydroxide/oxide phases with only minor amounts of carbonate, sulfate, silicate, or phosphate phases. None of the predicted solid phases contained nitrate or nitrite, indicating that these components were completely soluble for all of the simulations. Although both the Felmy and Nuclear databases predict many of the same phases, there are some significant differences that impact the final calculated supernatant concentrations. These differences center on the aluminum, phosphate, and fluoride components.

In the case of aluminum, the Nuclear database predicts gibbsite should be the stable phase in all steps of the sludge processing. In contrast, the Felmy database predicts that boehmite should be stable in the critical leach step. For phosphate, the Nuclear database predicts the formation of very insoluble  $\text{LaPO}_4 \cdot 2\text{H}_2\text{O}$  and hydroxyapatite. In contrast, the Felmy database predicts that the phosphate will be completely soluble. Use of the Nuclear database also results in predictions of the formation of a very insoluble  $\text{CaF}_2$  phase, whereas use of the Felmy database predicts the initial formation of the more soluble double salt  $\text{NaF} \cdot \text{Na}_2\text{SO}_4$ . These differences in predicted phase behavior result in significant differences in predicted supernatant concentrations, as described in the following sections.

**Table 2.1. Summary of Predicted Solid Phases Formed During the Processing of Tank AZ-101 Slurry. The term “Not included” indicates no thermodynamic data for this component are in the indicated database.**

Analytes	Nuclear database	Felmy database
Al	Gibbsite (Al(OH) <sub>3</sub> )	Gibbsite (Al(OH) <sub>3</sub> ), Boehmite
Ba	BaSO <sub>4</sub>	BaSO <sub>4</sub>
Ca	CaF <sub>2</sub> , Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub>	Pirssonite, CaCO <sub>3</sub> , Gaylussite
Cd	Cd(OH) <sub>2</sub>	Not included
CO <sub>3</sub> <sup>2-</sup>	SrCO <sub>3</sub> , CaCO <sub>3</sub>	SrCO <sub>3</sub> , CaCO <sub>3</sub> , Gaylussite
Cr	Cr <sub>2</sub> O <sub>3</sub>	Cr(OH) <sub>3</sub>
F <sup>-</sup>	CaF <sub>2</sub>	NaFNa <sub>2</sub> SO <sub>4</sub>
Fe	FeOOH	FeOOH
K	KAlSiO <sub>4</sub>	KNaCO <sub>3</sub> ·6H <sub>2</sub> O
La	LaPO <sub>4</sub> ·2H <sub>2</sub> O	Not included
Mn	Mn(OH) <sub>2</sub>	Mn(OH) <sub>2</sub>
Na	NaAlSiO <sub>4</sub> , Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> , NaAlSiO <sub>4</sub>	Pirssonite, Gaylussite
Nd	NdPO <sub>4</sub> ·2H <sub>2</sub> O	Nd(OH) <sub>3</sub>
Ni	Ni(OH) <sub>2</sub>	Ni(OH) <sub>2</sub>
Oxalate	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Not included
Pb	Pb(OH) <sub>2</sub>	Pb(OH) <sub>2</sub>
PO <sub>4</sub> <sup>3-</sup>	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub> , LaPO <sub>4</sub> ·2H <sub>2</sub> O	Completely soluble
Si	KAlSiO <sub>4</sub> , NaAlSiO <sub>4</sub>	No alumino-silicates in database
SO <sub>4</sub> <sup>2-</sup>	BaSO <sub>4</sub>	NaFNa <sub>2</sub> SO <sub>4</sub> , BaSO <sub>4</sub>
Sr	SrCO <sub>3</sub>	SrCO <sub>3</sub>
U	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	Not included
Zr	ZrO <sub>2</sub>	Not included

## 2.2 Aluminum Predictions

Figure 2.1 presents a comparison of the predicted and observed Al concentrations in the supernatant solutions as a function of processing step. There are several important factors that are apparent from the results shown in Figure 2.1.

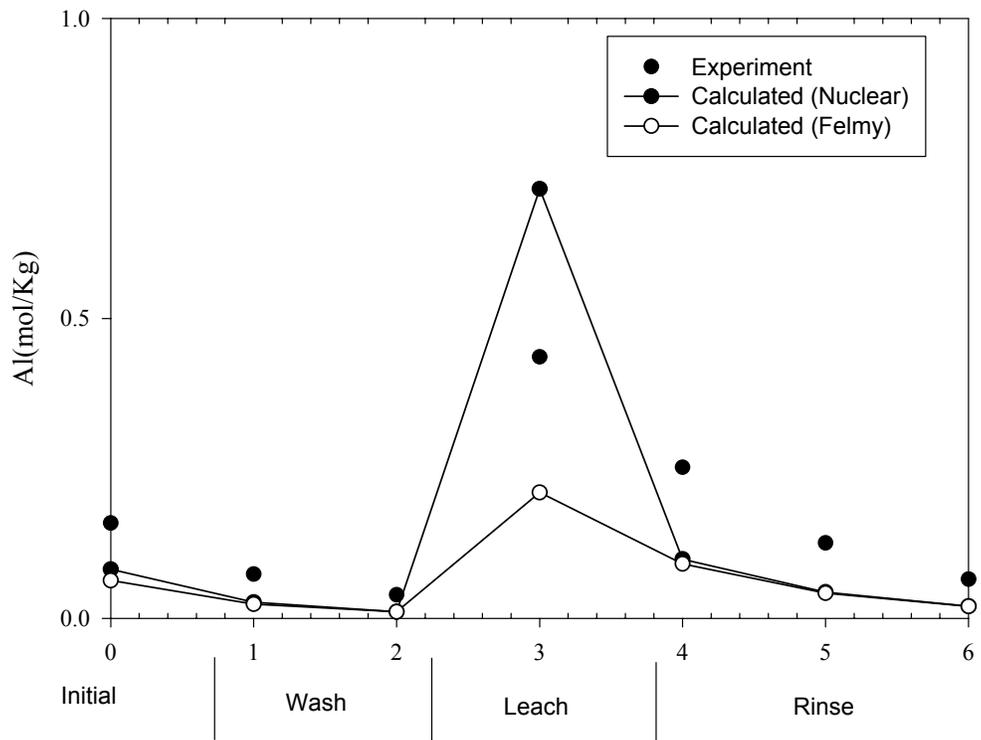
First, the experimental Al concentrations in the initial solutions and in the two wash solutions (samples AZ-A, AZ-C, and AZ-E, Geeting et al. 2002) are higher than the model predictions. These higher aluminum concentrations indicate that the solutions are initially oversaturated with respect to the predicted stable phase, gibbsite. These results indicate that there is a potential for

gibbsite precipitation from these solutions. Use of both the Felmy and Nuclear databases results in similar predictions of aqueous Al concentrations and the stable phase being gibbsite.

Second, the addition of 3M NaOH and heating the solutions to 85°C in the leach step results in the dissolution of significant amounts of Al from the solid phase. The two different models predict different results for these leach solutions. The Nuclear database predicts that gibbsite should remain stable and that the dissolved Al concentrations should be higher than experimentally observed. The Felmy database predicts boehmite should be stable and therefore predicts less Al in solution than experimentally observed. Interestingly, if the formation of boehmite is suppressed in the Felmy database, then the results are much closer to the predictions using the Nuclear database (i.e., the gibbsite should be completely or nearly completely soluble). So, both of the models predict that any gibbsite initially present should be soluble. The Felmy database predicts that boehmite will be more insoluble and, depending upon the exact base concentration and solid ratios, may not dissolve in the leach step<sup>(1)</sup>. The difference in chemical stability between boehmite and gibbsite means that the removal of Al will be dependent upon the initial gibbsite to boehmite ratio. Specifically, if the initial slurry contains large quantities of gibbsite, then the efficiency of the removal process should be significantly greater than if the initial solids are predominantly the more refractory boehmite. Following the leach step, both models again show similar predictions for the rinse steps (i.e., re-precipitation of Al from the leach step as gibbsite). The characterization data for the solids following the rinse step (Buck et al. 2002) shows that both gibbsite and boehmite are present. Our modeling results agree with this observation but also support the idea that the gibbsite should have dissolved in the leach step and then re-precipitated in the rinse steps. The boehmite probably went entirely through the wash, leach, and rinse steps intact. The rinse steps do result in the removal of significant amounts of dissolved Al, which reduces the tendency for gibbsite precipitation later in the process stream.

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1 The difference in Al predictions is due mainly to the fact that in the Nuclear database the temperature range for boehmite limits formation of the solid to above 100°C. If this temperature range is expanded or removed in the Nuclear database, ESP predicts boehmite precipitation at the leach temperature of 85°C using either database.

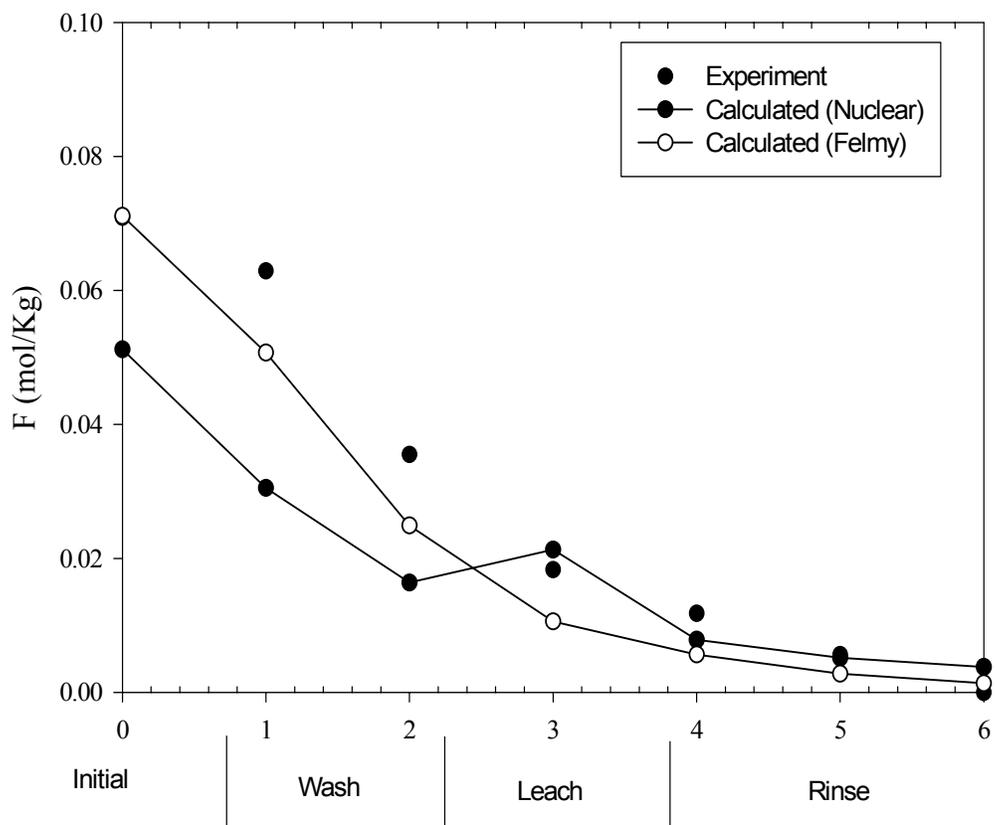


**Figure 2.1. Experimental and Calculated Dissolved Al Concentrations**

The numbers 0-6 on the x-axis correspond to the initial (0), first wash (1), second wash (2), leach (3), first rinse (4), second rinse (5), and third rinse (6) steps. All concentrations are in moles/Kg of solution.

### 2.3 Fluoride Predictions

Predictions of the dissolved fluoride concentrations, Figure 2.2, show some significant differences between the models. Use of the Felmy database results in a near exact prediction of the dissolved F concentration in the initial solution. This concentration is determined by equilibrium with the  $\text{NaF}\cdot\text{Na}_2\text{SO}_4$  double salt. The small amount of the initially precipitated  $\text{NaF}\cdot\text{Na}_2\text{SO}_4$  double salt then dissolves in the first wash step. In contrast, use of the Nuclear database predicts the formation of an insoluble  $\text{CaF}_2$ , which lowers the calculated dissolved fluoride concentration below the observed experimental values. The initially precipitated  $\text{CaF}_2$  then does not completely dissolve until the leach step. The experimental data do not support the calculations using the Nuclear database. It would appear that the initial solutions are in equilibrium with the  $\text{NaF}\cdot\text{Na}_2\text{SO}_4$  double salt, and the small amount of this initial phase is removed in the first wash.



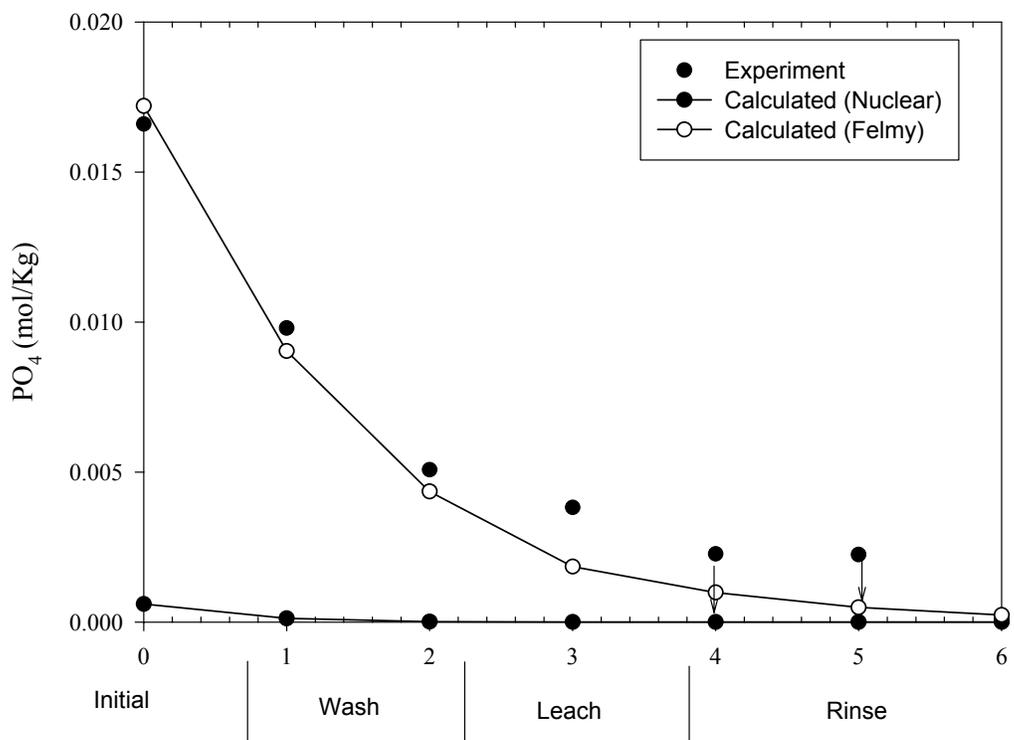
**Figure 2.2. Experimental and Calculated Dissolved  $F^-$  Concentrations**

The numbers 0-6 on the x-axis correspond to the initial (0), first wash (1), second wash (2), leach (3), first rinse (4), second rinse (5), and third rinse (6) steps. All concentrations are in moles/Kg of solution.

## 2.4 Phosphate Predictions

The calculations of dissolved phosphate show dramatic differences between the two different models. Use of the Felmy database predicts that all of the initial phosphate is soluble. This prediction matches the experimental results very closely. Use of the Nuclear database results in totally erroneous predictions. The calculated phosphate concentrations using the Nuclear database are much lower than the experimental values. These low predicted phosphate concentrations result from the predicted initial formation of hydroxyapatite followed by the predicted formation of a very insoluble  $LaPO_4 \cdot 2H_2O$  phase in the wash and later steps. Hydroxyapatite is known to be an insoluble phase, but the kinetics of precipitation is also known to be very slow. This lack of equilibrium probably results in the initial erroneous prediction. In the case of the  $LaPO_4 \cdot 2H_2O$  phase, the error appears to be in the solubility product since the

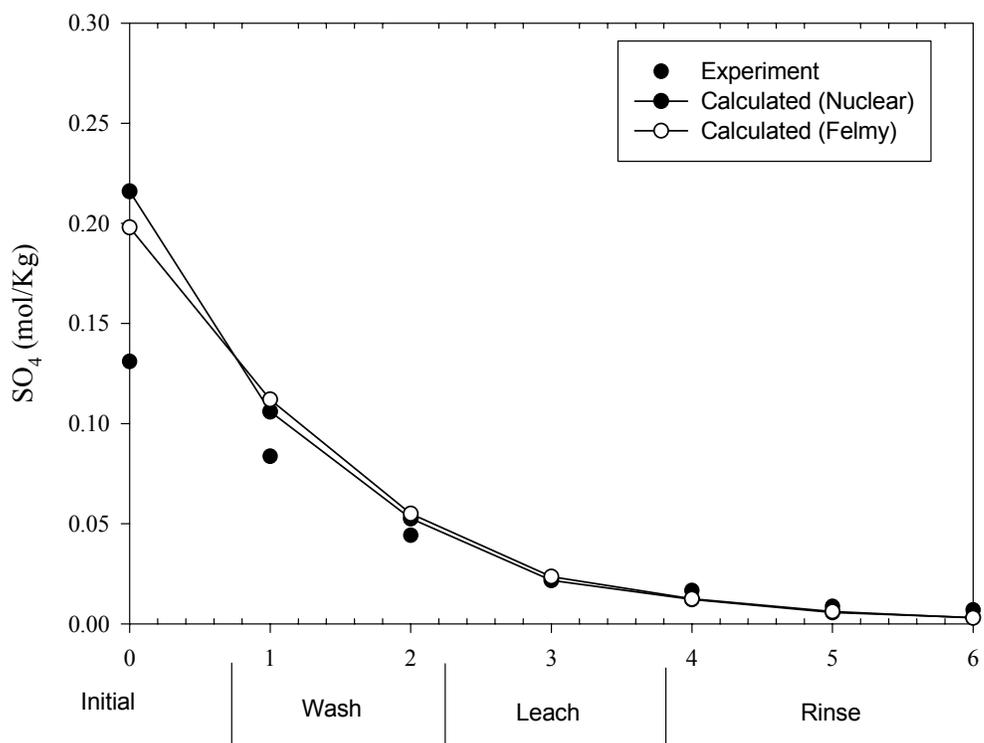
calculated dissolved lanthanum (La) concentration is extremely low ( $\sim 10^{-18}$  M). In any event, use of the Felmy database appears to give quite useful predictions.



**Figure 2.3. Experimental and Calculated Dissolved  $\text{PO}_4^{3-}$  Concentrations**  
 The numbers 0-6 on the x-axis correspond to the initial (0), first wash (1), second wash (2), leach (3), first rinse (4), second rinse (5), and third rinse (6) steps. All concentrations are in moles/Kg of solution. Arrows at 4 and 5 indicate less than values in the experimental data.

## 2.5 Sulfate Predictions

The predictions of the dissolved sulfate concentration are very close between the two models since the majority of the sulfate is predicted to be soluble. Both models predict the formation of insoluble  $\text{BaSO}_4$ , but the total Ba in the waste is too small to remove much sulfate. Use of the Felmy database does result in the predicted formation of small amounts of the  $\text{NaF}\cdot\text{Na}_2\text{SO}_4$  double salt, and this does result in the calculated soluble concentrations of sulfate being somewhat lower than the calculated values using the Nuclear database (Figure 2.4). However, the total amount of precipitated  $\text{NaF}\cdot\text{Na}_2\text{SO}_4$  double salt is not very large. Both models do overpredict the amount of soluble sulfate in the initial and wash solutions. This overprediction is most likely due to an analytical overestimate of the initial sulfate in the slurry.

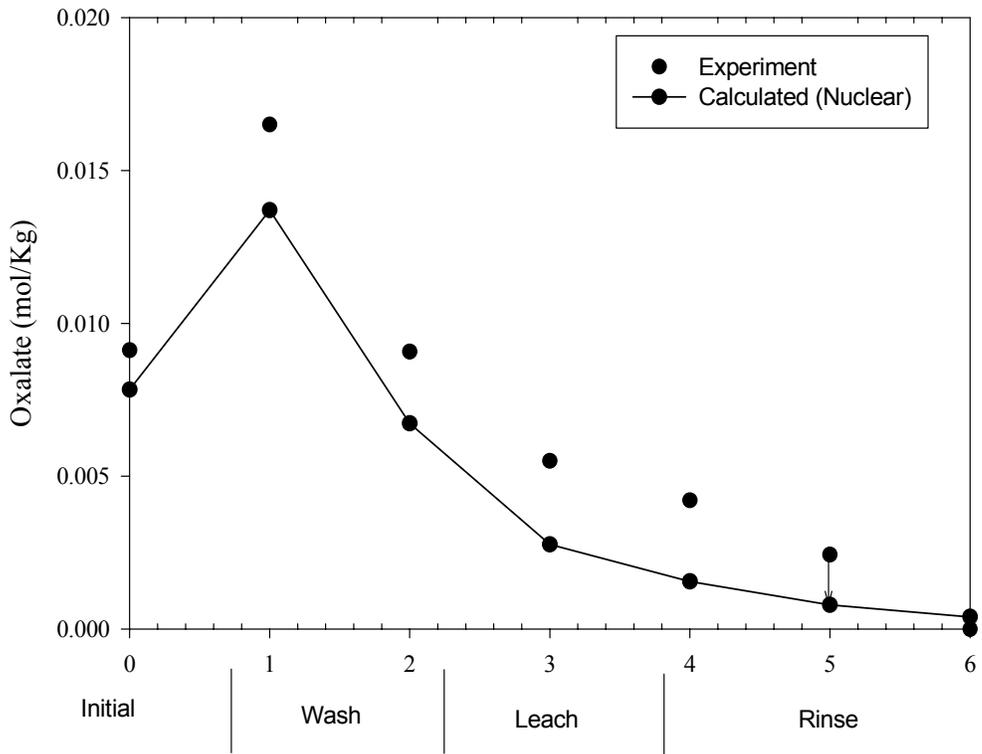


**Figure 2.4. Experimental and Calculated Dissolved  $\text{SO}_4^{2-}$  Concentrations**

The numbers 0-6 on the x-axis correspond to the initial (0), first wash (1), second wash (2), leach (3), first rinse (4), second rinse (5), and third rinse (6) steps. All concentrations are in moles/Kg of solution.

## 2.6 Oxalate Predictions

The dissolved oxalate concentrations in the slurry processing steps follow a different trend from any of the other constituents in that the dissolved concentration of oxalate actually increases in the first wash solution over that in the initial solution (Figure 2.5). Modeling of these solutions using the Nuclear database (oxalate is not included in the Felmy database) shows that this increase occurs as a result of dissolution of initially present  $\text{Na}_2\text{C}_2\text{O}_4$  in the first wash. The first wash significantly dilutes the  $\text{Na}^+$  concentration, resulting in the dissolution of the precipitated  $\text{Na}_2\text{C}_2\text{O}_4$ . The model then predicts that the oxalate is simply washed out by the subsequent processing steps. The model underpredicts the dissolved concentrations slightly in the later processing steps. This probably results from a slight underestimate of the initial total oxalate in the slurry. However, on an overall basis, the Nuclear database model appears to match the experimental trend quite closely.



**Figure 2.5. Experimental and Calculated Dissolved Oxalate Concentrations**  
 The numbers 0-6 on the x-axis correspond to the initial (0), first wash (1), second wash (2), leach (3), first rinse (4), second rinse (5), and third rinse (6) steps. All concentrations are in moles/Kg of solution.

## 2.7 Predictions of Other Components

There are several other components in the solution that are worth mentioning but which do not significantly change during the entire slurry leaching process.

From a processing standpoint, probably the most significant of these is strontium (Sr). Both models predict that the Sr should be present predominantly in the precipitates as relatively insoluble  $\text{SrCO}_3$ . In general, use of the Felmy database predicts slightly higher concentrations in solution owing to the inclusion of aqueous strontium carbonate complexes. However, the majority of the Sr is predicted to be in the solid phase. For example, the predicted solid to solution ratio for Sr in the second wash step is 375:1 on a molar basis.

The concentrations of La and neodymium (Nd) are also worth mentioning since their chemical behavior can be analogous to the trivalent actinides americium (Am) and curium (Cm). Use of the Felmy database for Nd predicts solubilities on the order of  $10^{-8}$  M, which is close to the experimental values under basic solutions in equilibrium with the hydroxide phases (Felmy et

al. 2001). Use of the Nuclear database results in much lower predictions ( $10^{-11}$  to  $10^{-18}$  M) as a result of a predicted equilibrium with phosphate phases. As was previously shown for phosphate, such low solubilities do not correlate with the experimental phosphate concentrations. The calculated solubility of U using the Nuclear database is also quite low for a U(VI) compound ( $10^{-8}$  to  $10^{-13}$  M). Uranium (U) is not in the Felmy database so no direct comparison is possible. Several other elements, Ba, Ca, Cd, Fe, Pb, Ni, and Zr, are calculated to be in equilibrium with the hydroxide/oxide phases at low total concentrations. Prediction of such low concentrations appears to be qualitatively correct. A quantitative comparison between model and experiment is hindered since the experimental concentrations for these elements are often below the detection limit of the analytical instrument. The chromium (Cr) predictions are based upon a 50:50 split between Cr(VI) and Cr(III). The 50:50 split is based upon the 56% soluble chromium found in the wash solutions (Geeting et al. 2002). The soluble chromium was assumed to be chromate Cr(VI).

### 3.0 Summary of AZ-101 Processing Simulation

In summary, the AZ-101 sludge washing process described by Geeting et al. (2002) was simulated with ESP using separate split and mix blocks. The exact mass additions or withdraws detailed by Geeting et al. were implemented. The simulations therefore were based solely upon the initial masses of slurry and supernatant, subsequent mass addition or withdraws, and the thermodynamic simulations.

The results showed that overall the models gave a quite satisfactory representation of the experimental data for the principal components in the slurry. The initial solids in the slurry were dominated by metal hydroxides/oxides with small amounts of carbonates and sulfates. The major anions, nitrate and nitrite, were undersaturated with respect to any possible precipitates during the entire leach process. The initial wash solution did remove small amounts of precipitated fluoride, sulfate, and oxalate; but it did not remove any of the major amounts of the initial oxide/hydroxide solids. The leach solution should have dissolved all of the initially present gibbsite. However, any initially present boehmite appears to be thermodynamically stable and remains unleachable. The final rinse steps did remove significant amounts of Al that was solubilized in the leach step. The dissolved Al in the rinse steps was significantly oversaturated with respect to gibbsite. Gibbsite formation does present a possible post-precipitation issue. In general, use of the Felmy database gave more realistic predictions of the final dissolved concentrations than use of the Nuclear database. Both models did give qualitatively accurate predictions of several minor components (Ba, Ca, Cd, Fe, Pb, Ni, Sr, and Zr). However, several others, U, La, Nd, and  $\text{PO}_4^{3-}$ , were predicted to be at extremely low concentration using the Nuclear database.

## 4.0 Recommendations

This section proposes a series of improvements that the modeling activities indicate would better optimize the overall processing of AZ-101 sludge.

**Recommendation #1:** Eliminate the second wash step and possibly the first wash step as well. The second wash step really does nothing except dilute already soluble constituents (Na, NO<sub>3</sub>, NO<sub>2</sub>, etc.). The first wash does dissolve small amounts of precipitates (i.e., Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, NaF•Na<sub>2</sub>SO<sub>4</sub>) but is mainly a simple dilution step as well. To test the validity of removing both wash steps, the ESP simulations as depicted in (Figure 1.1) were modified by eliminating the two wash steps. This resulted in the caustic leach solutions being added directly to the initial slurry without washing. This direct addition of NaOH did result in an increase in Na<sup>+</sup> concentration in the leach step over the current two wash cases (see Table A.8 in the Appendix). However, the initially present Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and NaF•Na<sub>2</sub>SO<sub>4</sub> dissolved in the leach solution owing to the dilution of the oxalate, fluoride, and sulfate by the added caustic. This dissolution occurred despite the higher Na<sup>+</sup> concentration. The initially present nitrate and nitrite were also diluted by the NaOH addition. Notice that the aluminum solubility was predicted to be higher without the initial washes than with them, and with both Nuclear and Felmy databases. Also, the precipitation tendency for both gibbsite and boehmite is predicted to be lower (see bottom of Table A.8). This is due to the fact that the solubility of aluminum increases with ionic strength or, in this case, with sodium concentration. So, unless the higher Na<sup>+</sup> concentration is a problem, it appears that both wash steps could be removed.

**Recommendation #2:** Test increasing the reaction time in the leach step. The models predict that the initially present gibbsite should be completely soluble in the leach step, yet Buck et al. (2002) found gibbsite present in the solids following the final rinse. This gibbsite could have been re-precipitated in the rinse steps or may not have had time to completely dissolve in the leach solution. This latter possibility should be tested.

**Recommendation #3:** Test a higher NaOH concentration in the leach. The models indicate that boehmite is less soluble than gibbsite in the leach step. If this is the case, the only way to remove the insoluble boehmite is to increase the NaOH concentration. Our models indicate that the NaOH concentration would need to be increased to 5mol/Kg at 85°C to dissolve the entire Al, if all of the Al were present as boehmite. This is obviously a worst case scenario since significant amounts of the initially-present Al are expected to be present as gibbsite. In order to do a more exact calculation, the initial ratio of boehmite to gibbsite must be known. In testing higher OH<sup>-</sup> concentrations, the leach times may also need to be varied as described in Recommendation #2.

**Recommendation #4:** Retain the rinse steps, or better yet, use a higher NaOH concentration in the rinse. The rinse steps perform the valuable function of removing excess dissolved Al. The dissolved aluminum has the potential to re-precipitate somewhere down the process stream,

therefore the rinse steps are critical and should be retained. Higher NaOH concentrations should also be investigated in the rinse solutions, since these solutions are predicted to be supersaturated in Al. Use of a higher NaOH concentration in the rinse would result in a solution that is undersaturated with respect to gibbsite and thereby avoid potential Al re-precipitation problems in the LAW stream (permeate).

**Recommendation #5:** Conduct a definitive thermodynamic and kinetic study of the behavior of aluminum in relevant electrolyte solutions and tank wastes. The chemistry of aluminum is clearly a concern for the processing of these tank wastes owing to the potential for post-precipitation. Unfortunately, definitive studies on the solubility controlling solids and the kinetics of precipitation of these phases have not been done. Unless a thorough and definitive study is conducted, the issue of post-precipitation of aluminum will remain.

## 5.0 References

- Buck, E.C., A.P. Poloski, B.W. Arey, J.G.H. Geeting, E.D. Jenson, and B.K. McNamara. 2002. *Characterization of Hanford Tanks 241-AN-102 and AZ-101 Washed Solids with X-Ray Diffraction, Scanning Electron Microscopy, and Light-Scattering Particle Analysis*. WTP-RPT-076, Battelle – Pacific Northwest Division, Richland, WA.
- Felmy A.R. 2000. Thermodynamic Modeling of Sr/TRU Removal. PNWD-3044, Battelle - Pacific Northwest Division, Richland, WA.
- Felmy, A.R., J.R. Rustad, M.J. Mason, and R. de la Bretonne. (1994). "A Chemical Model for the Major Electrolyte Components of the Hanford Waste Tanks: The Binary Electrolytes in the System: Na-NO<sub>3</sub>-NO<sub>2</sub>-SO<sub>4</sub>-CO<sub>3</sub>-F-PO<sub>4</sub>-OH-Al(OH)<sub>4</sub>-H<sub>2</sub>O." TWRS-PP—94-090. The Westinghouse Hanford Co., Richland, WA.
- Felmy, A.R., D.A. Dixon, Z. Wang, A.G. Joly, J.R. Rustad, and M.J. Mason. 2001. The Aqueous Complexation of Eu(III) with Organic Chelates at High Base Concentration: Molecular and Thermodynamic Modeling Results. ACS Symposium Series 778 Chapter 5 pp 63-82.
- Felmy A.R. and G.T. MacLean. 2001. *Development of an Enhanced Database for the ESP Model: The Fluoride and Phosphate Components*. PNWD-3120, Battelle – Pacific Northwest Division, Richland, WA.
- Geeting, J.G.H., K.P. Brooks, R.T. Hallen, L.K. Jagoda, A.P. Poloski, D.R. Weier, and R.D. Scheele. 2002. *Filtration, Washing, and Caustic Leaching of Hanford AZ-101 Sludge*. PNWD-3206, Battelle – Pacific Northwest Division, Richland, WA.
- OLI Systems Inc. 2002. *Environmental Simulation Program (ESP)*, version 6.6. Morris Plains, NJ.
- Pitzer K.S. 1973. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *Journal of Physical Chemistry* **77**, 268-277.
- Pitzer K.S. 1991. *Activity Coefficients in Electrolyte Solutions*, 2nd Edition. CRC Press, Boca Raton, FL.
- Sanders, S., R. Young, and A.R. Felmy. 2001. Inclusion of Pitzer Equations in the ESP Computer Model (Beta Version). Tanks Focus Area Milestone Report B.3-1.

Urie, M.W., G.M. Mong, P.R. Bredt, A.P. Poloski, J.A. Campbell, R.D. Scheele, O.T. Farmer, C.Z. Soderquist, S.K. Fiskum, R.G. Swoboda, L.R. Greenwood, M.P. Thomas, E.W. Hoppe, and J.J. Wagner. 2002. *Chemical Analysis and Physical Property Testing of 241-AZ-101 Tank Waste—Supernatant and Centrifuged Solids*. PNWD-3215, Battelle – Pacific Northwest Division, Richland, WA.

## **Appendix A: Detailed Experimental and Modeling Comparison**

This section presents detailed comparisons between the experimental data on slurry leaching of tank AZ-101 samples and the thermodynamic modeling calculations. Modeling calculations are presented for the total concentrations in solution, the most important aqueous species in the calculations, and the most important solid phases. All reported concentrations are for liquid solutions and are in units of moles/Kg of solution.

**Table A.1. Experimental (AZ-A) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 initial slurry. Experimental data from Geeting et al. (2002). Step (0) in Figures 2.1-2.5.**

AZ-A (sample) or Starting Liquid (simulation)								
Analytes	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	1.97E-01	1.59E-01	8.20E-02	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>	6.32E-02	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>
Ba			9.90E-07	Ba	BaSO <sub>4</sub>	3.97E-06	Ba	Barite
Br	1.26E-02	1.02E-02						
Ca			4.27E-06	CaCO <sub>3</sub>	CaF <sub>2</sub>	4.55E-05	Ca(CO <sub>3</sub> ) <sub>2</sub>	Pirssonite
Cd			8.18E-05	Cd(OH) <sub>4</sub>	Cd(OH) <sub>2</sub>			
Cl								
CO <sub>3</sub>	7.02E-01	5.66E-01	5.51E-01	CO <sub>3</sub> ,NaCO <sub>3</sub>	SrCO <sub>3</sub>	4.91E-01	CO <sub>3</sub>	SrCO <sub>3</sub>
Cr	1.20E-02	9.68E-03	1.03E-02	CrO <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>	1.14E-02	CrO <sub>4</sub>	Cr(OH) <sub>3</sub>
F	8.79E-02	7.09E-02	5.12E-02	F,NaF	CaF <sub>2</sub>	7.11E-02	F	NaFNa <sub>2</sub> SO <sub>4</sub>
Fe			1.23E-07	FeIII(OH) <sub>4</sub>	FeOOH	6.06E-08	Fe(OH) <sub>4</sub>	FeOOH
K	1.03E-01	8.33E-02	7.72E-02	K	KAISiO <sub>4</sub>	9.03E-02	K	
La			8.03E-15	La(OH) <sub>4</sub>	LaPO <sub>4</sub> .2H <sub>2</sub> O			
MoO <sub>4</sub>	9.05E-04	7.30E-04						
Mn			2.00E-04	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>	4.79E-06	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>
Na	4.46E+00	3.60E+00	4.08E+00	Na	NaAlSiO <sub>4</sub>	4.07E+00	Na	Pirssonite
Nd			1.74E-11	Nd(OH) <sub>4</sub>	NdPO <sub>4</sub> .2H <sub>2</sub> O	2.52E-08	Nd(OH) <sub>4</sub>	Nd(OH) <sub>3</sub>
Ni			1.24E-05	Ni(OH) <sub>3</sub>	Ni(OH) <sub>2</sub>	1.35E-10	NiOH	Ni(OH) <sub>2</sub>
NO <sub>2</sub>	1.86E+00	1.50E+00	1.13E+00	NO <sub>2</sub>		1.14E+00	NO <sub>2</sub>	
NO <sub>3</sub>	1.16E+00	9.32E-01	7.49E-01	NO <sub>3</sub> ,NaNO <sub>3</sub>		7.55E-01	NO <sub>3</sub>	
OH			5.39E-01	OH	Al(OH) <sub>3</sub>	5.25E-01	OH	Al(OH) <sub>3</sub>
Oxalate	1.13E-02	9.12E-03	7.84E-03	Oxalate	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>			
Pb			1.77E-06	HPbO <sub>2</sub>	Pb(OH) <sub>2</sub>	2.72E-06	Pb(OH) <sub>3</sub>	Pb(OH) <sub>2</sub>
PO <sub>4</sub>	2.06E-02	1.66E-02	6.05E-04	PO <sub>4</sub>	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub>	1.72E-02	PO <sub>4</sub>	
Si	7.73E-03	6.23E-03	2.15E-02	NaHSiO <sub>3</sub> ,H <sub>2</sub> SiO <sub>4</sub>	KAISiO <sub>4</sub>	8.03E-02	H <sub>2</sub> SiO <sub>4</sub>	
SO <sub>4</sub>	1.62E-01	1.31E-01	2.16E-01	SO <sub>4</sub>	BaSO <sub>4</sub>	1.98E-01	SO <sub>4</sub>	NaFNa <sub>2</sub> SO <sub>4</sub>
Sr			4.91E-07	Sr,SrOH	SrCO <sub>3</sub>	1.00E-05	SrCO <sub>3</sub>	SrCO <sub>3</sub>
U			3.53E-10	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>			
Zr			9.43E-05	Zr(OH) <sub>5</sub>	ZrO <sub>2</sub>			

**Table A.2. Experimental (AZ-C) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 first wash. Experimental data from Geeting et al. (2002). Step (1) in Figures 2.1-2.5.**

AZ-C (sample) or Wash 1 Filtrate (simulation)								
Analytes	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	8.71E-02	7.38E-02	2.71E-02	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>	2.40E-02	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>
Ba			5.93E-07	Ba	BaSO <sub>4</sub>	1.82E-06	Ba	Barite
Br	5.38E-03	4.56E-03	4.37E-04	Br				
Ca	2.50E-04	2.11E-04	7.50E-06	CaCO <sub>3</sub>	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub>	3.70E-05	Ca	Calcite
Cd			7.06E-06	Cd(OH) <sub>4</sub>	Cd(OH) <sub>2</sub>			
Cl								
CO <sub>3</sub>	3.34E-01	2.83E-01	2.83E-01	CO <sub>3</sub> ,NaCO <sub>3</sub>	SrCO <sub>3</sub>	2.76E-01	CO <sub>3</sub>	Calcite
Cr	4.17E-03	3.54E-03	5.03E-03	CrO <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>	5.12E-03	CrO <sub>4</sub>	Cr(OH) <sub>3</sub>
F	7.42E-02	6.29E-02	3.05E-02	F,NaF	CaF <sub>2</sub>	5.09E-02	F	
Fe	2.15E-05	1.82E-05	3.42E-08	FeIII(OH) <sub>4</sub>	FeOOH	2.25E-08	Fe(OH) <sub>4</sub>	FeOOH
K	4.30E-02	3.64E-02	3.49E-02	K	KAlSiO <sub>4</sub>	4.54E-02	K	
La	0.00E+00	0.00E+00	8.79E-17	La(OH) <sub>4</sub>	LaPO <sub>4</sub> .2H <sub>2</sub> O			
MoO <sub>4</sub>	4.11E-04	3.49E-04						
Mn			1.31E-05	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>	2.08E-06	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>
Na	1.84E+00	1.56E+00	2.15E+00	Na	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	2.18E+00	Na	
Nd			1.83E-13	Nd(OH) <sub>4</sub>	NdPO <sub>4</sub> .2H <sub>2</sub> O	9.46E-09	Nd(OH) <sub>4</sub>	Nd(OH) <sub>3</sub>
Ni			3.79E-06	Ni(OH) <sub>3</sub>	Ni(OH) <sub>2</sub>	3.94E-10	NiOH	Ni(OH) <sub>2</sub>
NO <sub>2</sub>	7.15E-01	6.06E-01	5.94E-01	NO <sub>2</sub>		5.93E-01	NO <sub>2</sub>	
NO <sub>3</sub>	4.73E-01	4.00E-01	3.91E-01	NO <sub>3</sub>		3.90E-01	NO <sub>3</sub>	
OH			2.95E-01	OH	Al(OH) <sub>3</sub>	2.83E-01	OH	Al(OH) <sub>3</sub>
Oxalate	1.94E-02	1.65E-02	1.37E-02	Oxalate				
Pb	1.35E-05	1.15E-05	6.16E-07	HPbO <sub>2</sub>	Pb(OH) <sub>2</sub>	7.88E-07	Pb(OH) <sub>3</sub>	Pb(OH) <sub>2</sub>
PO <sub>4</sub>	1.16E-02	9.82E-03	1.23E-04	PO <sub>4</sub>	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub>	8.84E-03	PO <sub>4</sub>	
Si	6.69E-03	5.67E-03	2.98E-02	NaHSiO <sub>3</sub>	KAlSiO <sub>4</sub>	3.75E-02	H <sub>2</sub> SiO <sub>4</sub>	
SO <sub>4</sub>	9.87E-02	8.36E-02	1.07E-01	SO <sub>4</sub>	BaSO <sub>4</sub>	1.12E-01	SO <sub>4</sub>	Barite
Sr			3.85E-07	Sr,SrOH	SrCO <sub>3</sub>	3.36E-06	Sr	SrCO <sub>3</sub>
U			3.82E-09	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>			
Zr			5.16E-05	Zr(OH) <sub>5</sub>	ZrO <sub>2</sub>			

**Table A.3. Experimental (AZ-E) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 second wash. Experimental data from Geeting et al. (2002). Step (2) in Figures 2.1-2.5.**

AZ-E (sample) or Removed W 2 Filtrate (simulation)								
Analytes	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	4.48E-02	3.93E-02	1.10E-02	Al(OH)4	Al(OH)3	1.09E-02	Al(OH)4	Al(OH)3
Ba			4.44E-07	Ba	BaSO4	9.11E-07	Ba	BaSO4
Br	3.13E-03	2.74E-03	2.15E-04	Br				
Ca			1.60E-05	CaCO3	Ca5OH(PO4)3,CaF2	1.97E-05	Ca(CO3)2	CaCO3
Cd			1.87E-06	Cd(OH)3	Cd(OH)2			
Cl								
CO3	1.68E-01	1.48E-01	1.38E-01	CO3	SrCO3	1.36E-01	CO3	CaCO3
Cr	1.96E-03	1.72E-03	2.47E-03	CrO4	Cr2O3	2.54E-03	CrO4	Cr(OH)3
F	4.05E-02	3.55E-02	1.64E-02	F	CaF2	2.50E-02	F	
Fe	1.47E-05	1.29E-05	1.34E-08	Fe(OH)4	FeOOH	1.04E-08	Fe(OH)4	FeOOH
K	2.21E-02	1.94E-02	1.63E-02	K	KAlSiO4	2.23E-02	K	
La			8.89E-18	La(OH)4	LaPO4.2H2O			
MoO4	2.10E-04	1.84E-04		MoO4				
Mn			1.83E-06	Mn(OH)4	Mn(OH)2	5.70E-07	Mn(OH)4	Mn(OH)2
Na	9.05E-01	7.94E-01	1.08E+00	Na	Na2U2O7	1.07E+00	Na	
Nd			1.54E-14	Nd(OH)4	NdPO4.2H2O	4.20E-09	Nd(OH)4	Nd(OH)3
Ni			1.44E-06	Ni(OH)3	Ni(OH)2	7.68E-10	NiOH	Ni(OH)2
NO2	3.50E-01	3.07E-01	2.92E-01	NO2		2.91E-01	NO2	
NO3	2.16E-01	1.90E-01	1.92E-01	NO3		1.91E-01	NO3	
OH			1.52E-01	OH	Al(OH)3	1.47E-01	OH	Al(OH)3
Oxalate	1.03E-02	9.07E-03	6.73E-03	Oxalate				
Pb			2.65E-07	HPbO2	Pb(OH)2	2.98E-07	Pb(OH)3	Pb(OH)2
PO4	5.79E-03	5.08E-03	1.49E-05	PO4	LaPO4.2H2O	4.34E-03	PO4	
Si	7.12E-03	6.25E-03	2.88E-02	NaHSiO3	KAlSiO4	1.84E-02	H2SiO4	
SO4	5.04E-02	4.42E-02	5.26E-02	SO4	BaSO4	5.51E-02	SO4	BaSO4
Sr			3.10E-07	Sr	SrCO3	1.82E-06	Sr	SrCO3
U			1.25E-08	UO2(CO3)3	Na2U2O7			
Zr			2.48E-05	Zr(OH)5	ZrO2			

**Table A.4. Experimental (AZ-G) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 leach solution. Experimental data from Geeting et al. (2002). Step (3) in Figures 2.1-2.5.**

AZ-G (sample) or Leach Filtrate (simulation)								
Analytes	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	5.41E-01	4.36E-01	7.16E-01	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>	2.18E-01	Al(OH) <sub>4</sub>	Boehmite
Ba			2.52E-05	Ba	BaSO <sub>4</sub>	3.56E-05	Ba	BaSO <sub>4</sub>
Br			8.84E-05	Br				
Ca			4.05E-05	CaOH	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub>	8.52E-10	Ca	Gaylussite
Cd			6.37E-04	Cd(OH) <sub>4</sub>	Cd(OH) <sub>2</sub>			
Cl	2.34E-02	1.89E-02						
CO <sub>3</sub>	9.66E-02	7.79E-02	4.98E-02	CO <sub>3</sub>	CaCO <sub>3</sub>	3.27E-02	CO <sub>3</sub>	Gaylussite
Cr	2.60E-03	2.09E-03	1.02E-03	CrO <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>	1.22E-03	CrO <sub>4</sub>	CrOH <sub>3</sub>
F	2.26E-02	1.83E-02	2.13E-02	F		1.06E-02	F	
Fe	4.83E-05	3.90E-05	8.92E-06	Fe(OH) <sub>4</sub>	FeOOH	7.10E-06	Fe(OH) <sub>4</sub>	FeOOH
K	1.28E-02	1.03E-02	1.63E-02	K		8.52E-07	K	KNaCarb <sub>6</sub>
La			4.86E-08	La(OH) <sub>4</sub>	LaPO <sub>4</sub> ·2H <sub>2</sub> O			
MoO <sub>4</sub>	1.15E-04	9.25E-05						
Mn			1.41E-04	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>	2.19E-04	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>
Na	2.64E+00	2.13E+00	2.73E+00	Na	NaAlSiO <sub>4</sub>	2.81E+00	Na	Gaylussite
Nd			2.30E-05	Nd(OH) <sub>4</sub>	NdPO <sub>4</sub> ·2H <sub>2</sub> O	8.00E-08	Nd(OH) <sub>4</sub>	Nd(OH) <sub>3</sub>
Ni			1.36E-06	Ni(OH) <sub>3</sub>	Ni(OH) <sub>2</sub>	5.65E-11	NiOH	Ni(OH) <sub>2</sub>
NO <sub>2</sub>	1.69E-01	1.37E-01	1.20E-01	NO <sub>2</sub>		1.24E-01	NO <sub>2</sub>	
NO <sub>3</sub>	1.06E-01	8.53E-02	7.92E-02	NO <sub>3</sub>		8.14E-02	NO <sub>3</sub>	
OH			1.65E+00	OH	Al(OH) <sub>3</sub>	2.24E+00	OH	Boehmite
Oxalate	6.82E-03	5.50E-03	2.77E-03	Oxalate				
Pb	4.63E-05	3.74E-05	5.82E-07	HPbO <sub>2</sub>	Pb(OH) <sub>2</sub>	7.63E-06	Pb(OH) <sub>3</sub>	Pb(OH) <sub>2</sub>
PO <sub>4</sub>	4.74E-03	3.82E-03	6.56E-07	PO <sub>4</sub>	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub>	1.85E-03	PO <sub>4</sub>	
Si	6.69E-03	5.40E-03	2.19E-03	NaHSiO <sub>3</sub> , H <sub>2</sub> SiO <sub>4</sub>	NaAlSiO <sub>4</sub>	7.83E-03	H <sub>2</sub> SiO <sub>4</sub>	
SO <sub>4</sub>	2.82E-02	2.28E-02	2.17E-02	SO <sub>4</sub>	BaSO <sub>4</sub>	2.35E-02	SO <sub>4</sub>	BaSO <sub>4</sub>
Sr			4.20E-06	SrOH	SrCO <sub>3</sub>	8.87E-06	Sr	SrCO <sub>3</sub>
U			4.60E-11	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>			
Zr	1.75E-05	1.41E-05	1.86E-05	Zr(OH) <sub>5</sub>	ZrO <sub>2</sub>			

**Table A.5. Experimental (AZ-I) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 first rinse solution. Experimental data from Geeting et al. (2002). Step (4) in Figures 2.1-2.5.**

AZ-I (sample) or Rinse 1 Filtrate (simulation)								
Analytes	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	2.93E-01	2.52E-01	9.89E-02	Al(OH)4	Al(OH)3	9.11E-02	Al(OH)4	Al(OH)3
Ba			2.07E-06	Ba	BaSO4	6.50E-06	Ba	Barite
Br	1.56E-03	1.35E-03	4.96E-05	Br				
Ca			1.46E-04	CaH2SiO4,CaOH	CA5OHPO43	6.24E-05	Ca	Calcite
Cd			4.84E-05	Cd(OH)4	Cd(OH)2			
Cl	1.66E-02	1.43E-02						
CO3	6.08E-02	5.24E-02	3.50E-02	CO3,NaCO3	SrCO3	4.79E-02	CO3	Calcite
Cr	1.35E-03	1.16E-03	5.72E-04	CrO4	Cr2O3	1.07E-03	CrO4	Cr(OH)3
F	1.37E-02	1.18E-02	7.83E-03	F,NaF	CaF2	5.66E-03	F	
Fe	2.51E-05	2.16E-05	1.21E-07	FeIII(OH)4	FeOOH	8.54E-08	Fe(OH)4	FeOOH
K	5.88E-03	5.07E-03	9.17E-03	K		1.15E-02	K	
La			6.11E-13	La(OH)4	LAOH3			
MoO4	5.64E-05	4.86E-05						
Mn			1.22E-04	Mn(OH)4	Mn(OH)2	4.17E-05	Mn(OH)4	Mn(OH)2
Na	1.47E+00	1.26E+00	1.56E+00	Na	NA2U2O7	1.55E+00	Na	
Nd			3.69E-09	Nd(OH)4	NdPO4.2H2O	3.47E-08	Nd(OH)4	Nd(OH)3
Ni			1.33E-05	Ni(OH)3	Ni(OH)2	8.89E-11	NiOH	Ni(OH)2
NO2	9.87E-02	8.51E-02	6.76E-02	NO2		6.60E-02	NO2	
NO3	6.43E-02	5.55E-02	4.45E-02	NO3,NaNO3		4.34E-02	NO3	
OH			1.21E+00	OH	Al(OH)3	1.22E+00	OH	Al(OH)3
Oxalate	4.89E-03	4.21E-03	1.56E-03	Oxalate				
Pb	2.27E-05	1.96E-05	2.32E-06	HPbO2	Pb(OH)2	2.75E-06	Pb(OH)3	Pb(OH)2
PO4	2.63E-03	2.27E-03	5.54E-07	PO4	Ca5OH(PO4)3	9.85E-04	PO4	
Si	6.41E-03	5.52E-03	2.34E-02	NaHSiO3,H2SiO4		4.17E-03	H2SiO4	
SO4	1.93E-02	1.66E-02	1.22E-02	SO4	BaSO4	1.25E-02	SO4	Barite
Sr			3.18E-06	Sr,SrOH	SrCO3	2.85E-06	Sr	SrCO3
U			1.09E-13	UO2(CO3)3	Na2U2O7			
Zr			1.99E-04	Zr(OH)5	ZrO2			

**Table A.6. Experimental (AZ-K) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 second rinse solution. Experimental data from Geeting et al. (2002). Step (5) in Figures 2.1-2.5.**

AZ-K (sample) or Rinse 2 Filtrate (simulation)								
Analytes	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	1.48E-01	1.26E-01	4.40E-02	Al(OH)4	Al(OH)3	4.22E-02	Al(OH)4	Al(OH)3
Ba			1.53E-06	Ba	BaSO4	3.16E-06	Ba	Barite
Br	1.56E-03	1.34E-03	2.53E-05	Br				
Ca			1.44E-04	CaH2SiO4	CA5OH(PO4)3	3.51E-05	Ca(CO3)2	Calcite
Cd			1.00E-05	Cd(OH)4	Cd(OH)2			
Cl	8.74E-03	7.47E-03						
CO3	2.58E-02	2.21E-02	1.21E-02	CO3	SrCO3	2.36E-02	CO3	Calcite
Cr	6.92E-04	5.92E-04	2.91E-04	CrO4	Cr2O3	3.49E-04	CrO4	Cr(OH)3
F	6.58E-03	5.62E-03	5.15E-03	F,NaF	CaF2	2.79E-03	F	
Fe	2.33E-05	1.99E-05	5.31E-08	FeIII(OH)4	FeOOH	4.03E-08	Fe(OH)4	FeOOH
K	2.81E-03	2.40E-03	4.68E-03	K	KAlSiO4	5.69E-03	K	
La			1.25E-13	La(OH)4	LaPO4.2H2O			
MoO4	2.92E-05	2.50E-05						
Mn			1.85E-05	Mn(OH)4	Mn(OH)2	9.21E-06	Mn(OH)4	Mn(OH)2
Na	6.96E-01	5.95E-01	7.93E-01	Na	NA2U2O7	7.62E-01	Na	
Nd			2.66E-10	Nd(OH)4	NdPO4.2H2O	1.59E-08	Nd(OH)4	Nd(OH)3
Ni			5.64E-06	Ni(OH)3	Ni(OH)2	1.64E-10	NiOH	Ni(OH)2
NO2	4.11E-02	3.51E-02	3.45E-02	NO2		3.25E-02	NO2	
NO3	3.11E-02	2.66E-02	2.27E-02	NO3,NaNO3		2.14E-02	NO3	
OH			6.37E-01	OH	Al(OH)3	6.04E-01	OH	Al(OH)3
Oxalate	2.84E-03	2.43E-03	7.93E-04	Oxalate				
Pb			1.07E-06	HPbO2	Pb(OH)2	1.10E-06	Pb(OH)3	Pb(OH)2
PO4	2.63E-03	2.25E-03	1.73E-07	PO4	Ca5OH(PO4)3	4.86E-04	PO4	
Si	5.06E-03	4.32E-03	1.19E-02	NaHSiO3,H2SiO4		2.06E-03	H2SiO4	
SO4	1.01E-02	8.63E-03	6.20E-03	SO4	BaSO4	6.16E-03	SO4	Barite
Sr			3.21E-06	Sr,SrOH	SrCO3	2.05E-06	SrCO3	SrCO3
U			9.97E-14	UO2(CO3)3	Na2U2O7			
Zr			1.01E-04	Zr(OH)5	ZrO2			

**Table A.7. Experimental (AZ-M) and calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 third rinse solution. Experimental data from Geeting et al. (2002). Step (6) in Figures 2.1-2.5.**

Analytes	AZ-M (sample) or Final Filtrate (simulation)							
	Sample Data		Process Nuclear	Dominant Aqueous Species	Dominant Solid(s)	Process Felmy	Dominant Aqueous Species	Dominant Solid(s)
	(mol/L)	(mol/kg aq)	(mol/kg aq)			(mol/kg aq)		
Al	7.64E-02	6.53E-02	2.03E-02	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>	2.17E-02	Al(OH) <sub>4</sub>	Al(OH) <sub>3</sub>
Ba	1.97E-06	1.68E-06	1.32E-06	Ba	BaSO <sub>4</sub>	2.06E-06	Ba	Barite
Br			1.27E-05	Br				
Ca			1.13E-04	CaH <sub>2</sub> SiO <sub>4</sub>	CaF <sub>2</sub> , CaCO <sub>3</sub>	2.68E-05	Ca	Calcite
Cd			3.21E-06	Cd(OH) <sub>3</sub>	Cd(OH) <sub>2</sub>			
Cl	7.19E-03	6.15E-03						
CO <sub>3</sub>	7.91E-02	6.76E-02	5.52E-03	CO <sub>3</sub>	CaCO <sub>3</sub>	1.17E-02	CO <sub>3</sub>	Calcite
Cr	3.67E-04	3.14E-04	1.46E-04	Cr(OH) <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>	1.69E-04	CrO <sub>4</sub>	Cr(OH) <sub>3</sub>
F			3.80E-03	F	CaF <sub>2</sub>	1.46E-03	F	
Fe	3.04E-05	2.60E-05	2.43E-08	Fe(OH) <sub>4</sub>	FeOOH	2.08E-08	Fe(OH) <sub>4</sub>	FeOOH
K			2.35E-03	K		2.86E-03	K	
La			9.85E-15	La(OH) <sub>4</sub>	LaPO <sub>4</sub> .2H <sub>2</sub> O			
MoO <sub>4</sub>	1.56E-05	1.34E-05						
Mn			3.64E-06	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>	2.13E-06	Mn(OH) <sub>4</sub>	Mn(OH) <sub>2</sub>
Na	3.76E-01	3.21E-01	3.98E-01	Na	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	3.97E-01	Na	
Nd			1.90E-11	Nd(OH) <sub>4</sub>	NdPO <sub>4</sub> .2H <sub>2</sub> O	8.10E-09	Nd(OH) <sub>4</sub>	Nd(OH) <sub>3</sub>
Ni			2.55E-06	Ni(OH) <sub>3</sub>	Ni(OH) <sub>2</sub>	2.69E-10	NiOH	Ni(OH) <sub>2</sub>
NO <sub>2</sub>	2.72E-02	2.32E-02	1.73E-02	NO <sub>2</sub>		1.70E-02	NO <sub>2</sub>	
NO <sub>3</sub>	2.09E-02	1.78E-02	1.14E-02	NO <sub>3</sub>		1.12E-02	NO <sub>3</sub>	
OH			3.22E-01	OH	Al(OH) <sub>3</sub>	3.16E-01	OH	Al(OH) <sub>3</sub>
Oxalate			3.98E-04	Oxalate				
Pb			5.07E-07	HPbO <sub>2</sub>	Pb(OH) <sub>2</sub>	5.15E-07	Pb(OH) <sub>3</sub>	Pb(OH) <sub>2</sub>
PO <sub>4</sub>	1.32E-04	1.13E-04	8.86E-08	PO <sub>4</sub>	Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub>	2.54E-04	PO <sub>4</sub>	
Si	5.16E-03	4.41E-03	5.99E-03	H <sub>2</sub> SiO <sub>4</sub>		1.07E-03	H <sub>2</sub> SiO <sub>4</sub>	
SO <sub>4</sub>	8.07E-03	6.90E-03	3.11E-03	SO <sub>4</sub>	BaSO <sub>4</sub>	3.22E-03	SO <sub>4</sub>	Barite
Sr			2.76E-06	Sr	SrCO <sub>3</sub>	1.89E-06	Sr	SrCO <sub>3</sub>
U			1.33E-13	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>			
Zr			5.01E-05	Zr(OH) <sub>5</sub>	ZrO <sub>2</sub>			

**Table A.8. Calculated component concentrations, dominant aqueous species, and dominant solids in the AZ-101 leach filtrate. Comparison with and without washing before leaching.**

Leach Filtrate with and without Preleach Washes (boehmite excluded)								
Analytes	Process Nuclear (2 Washes)	Dominant Solid(s)	Process Nuclear (No Washes)	Dominant Solid(s)	Process Felmy (2 Washes)	Dominant Solid(s)	Process Felmy (No Washes)	Dominant Solid(s)
	(mol/kg aq)		(mol/kg aq)		(mol/kg aq)		(mol/kg aq)	
Al	7.16E-01	Al(OH)3	8.09E-01	NaAlSiO4	7.42E-01		1.12E+00	
Ba	2.52E-05	BaSO4	2.02E-05	BaSO4	3.38E-05	BaSO4	7.09E-05	BaSO4
Br	8.84E-05		3.02E-04					
Ca	4.05E-05	Ca5OH(PO4)3,CaCO3	1.89E-05	CaCO3,Ca5OH(PO4)3	7.26E-10	Gaylussite	5.36E-10	Gaylussite
Cd	6.37E-04	Cd(OH)2	1.79E-03	Cd(OH)2				
CO3	4.98E-02	CaCO3	1.87E-01	CaCO3	3.39E-02	Gaylussite	5.47E-02	Gaylussite
Cr	1.02E-03	Cr2O3	3.48E-03	Cr2O3	1.15E-03	CrOH3	1.51E-03	CrOH3
F	2.13E-02		3.85E-02		1.03E-02		2.23E-02	
Fe	8.92E-06	FeOOH	1.25E-05	FeOOH	5.27E-06	FeOOH	8.76E-06	FeOOH
K	1.63E-02		3.45E-02		1.09E-06	KNaCarb6	6.10E-07	KNaCarb6
La	4.86E-08	LaPO4.2H2O	5.53E-08	LaPO4.2H2O				
Mn	1.41E-04	Mn(OH)2	4.05E-04	Mn(OH)2	1.23E-04	Mn(OH)2	1.80E-04	Mn(OH)2
Na	2.73E+00	NaAlSiO4	3.98E+00	NaAlSiO4	2.72E+00	Gaylussite	3.95E+00	Gaylussite
Nd	2.30E-05	NdPO4.2H2O	2.62E-05	NdPO4.2H2O	5.91E-08	Nd(OH)3	1.02E-07	Nd(OH)3
Ni	1.36E-06	Ni(OH)2	2.05E-06	Ni(OH)2	7.08E-11	Ni(OH)2	3.91E-11	Ni(OH)2
NO2	1.20E-01		4.11E-01		1.20E-01		1.48E-01	
NO3	7.92E-02		2.70E-01		7.89E-02		9.71E-02	
OH	1.65E+00	Al(OH)3	1.93E+00	FeOOH	1.64E+00	FeOOH	2.36E+00	FeOOH
Oxalate	2.77E-03		9.46E-03					
Pb	5.82E-07	Pb(OH)2	7.57E-07	Pb(OH)2	5.66E-06	Pb(OH)2	1.19E-05	Pb(OH)2
PO4	6.56E-07	Ca5OH(PO4)3	4.67E-06	Ca5OH(PO4)3	1.79E-03		2.20E-03	
Si	2.19E-03	NaAlSiO4	2.50E-03	NaAlSiO4	7.58E-03		9.33E-03	
SO4	2.17E-02	BaSO4	7.40E-02	BaSO4	2.27E-02	BaSO4	3.76E-02	BaSO4
Sr	4.20E-06	SrCO3	1.87E-06	SrCO3	3.15E-14	Sr(OH)2.8H2O	3.23E-14	Sr(OH)2.8H2O
U	4.60E-11	Na2U2O7	5.78E-10	Na2U2O7				
Zr	1.86E-05	ZrO2	1.93E-05	ZrO2				
IS	3.37		5.55		3.35		5.39	
GPT	0.72		0.51		0.74		0.61	
BPT	1.47		1.12		4.60		4.14	

IS = Ionic Strength

GPT = Gibbsite Precipitation Tendency (saturation = 1.0)

BPT = Boehmite Precipitation Tendency (saturation = 1.0)

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